UNIVERSITI PUTRA MALAYSIA

DETERMINATION OF TIN IN LEAD-BASE, COPPER-BASE AND IRON-BASE ALLOYS BY SPECTROPHOTOMETRY AND GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY

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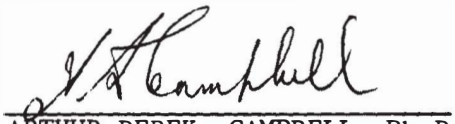

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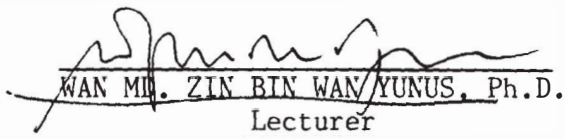

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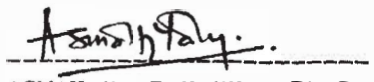

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DETERMINATION OF TIN IN LEAD-BASE, COPPER-BASE AND IRON-BASE ALLOYS BY SPECTROPHOTOMETRY AND GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY

by

UMI SIBYAN JAIS

A thesis submitted in partial fulfilment of the requirements for the degree of Master of Science in the Faculty of Science and Environmental Studies, Universiti Pertanian Malaysia

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April 1987

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Faculty : Science and Environmental Studies

This method development study of tin determination in alloys is divided into three parts, namely visible spectrophotometry, flameless atomic absorption spectrophotometry (FAAS) and classical methods. Visible spectrophotometry was chosen as the main technique because atomic absorption spectrophotometry by the flame mode (another popular method for tin) was known to give a lot of problems. However, FAAS using graphite furnace was also studied in this project since this appraoch was claimed to give better sensitivity.

The spectrophotometric method of determining tin in alloys using catechol violet and cetylpyridinium bromide is discussed in detail. Oxalic acid and lactic acid were found to speed up

the colour development process from approximately 2 hours to about 30 minutes. Calibration graph is rectilinier up to 1.6 ppm Sn at wavelength of maximum absorption (662 nm). The selectivity of the method was tested on lead tin-base white metals, brass, steel and foundary iron from Bureau of Analysed Samples (UK). Several approaches were tried involving masking and separation. Satisfactory results were obtained with method of separating major interferent by precipitation followed by masking.

Graphite furnace AAS method discussed the analysis of tin using Zr and W coated graphite tubes which were claimed to have improved the sensitivity of analysing Sn by this technique. The performance of these tubes was compared with the normal graphite and pyrollitically coated tubes. Both matrix modifier and masking agents were tried. Ammonium hydroxide was used as matrix modifier while lactic, ascorbic and tartaric acids which worked quite well with spectrophotometric technique were tried as masking agents. Atomisation from L'vov platform was also attempted with marked improvement in sensitivity. Precision, however, remains poor, R.S.D. at 5 - 6 percent.

Classical wet methods commonly applied to analysis of alloys namely titrimetry and gravimetry were also carried out as comparative techniques. For titrimetry, complexometric titration using EDTA and iodometric titration methods were

adopted while for gravimetry tin was precipitated as meta-stannic acid and determined as tin oxide (SnO_2).

Comparison with regard to accuracy, precision, sensitivity and simplicity of the various techniques was discussed. Among these, for the samples analysed in this project, spectrophotometric technique was found to be the most precise and accurate.

Abstrak tesis yang dikemukakan kepada Senat Universiti Pertanain Malaysia sebagai memenuhi sebahagian daripada syarat keperluan ijazah Master Sains

PENENTUAN TIMAH DALAM ALOI-ALOI PLUMBUM, KUPRUM DAN FERUM DENGAN KAEDAH SPEKTROMETRI TAMPAK DAN SPEKTROMETRI SERAPAN ATOM TANPA NYALAAN

oleh

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Kajian penentuan timah dalam aloi ini terbahagi kepada tiga bahagian. Ujikaji yang terpenting sekali ialah untuk mendapatkan kaedah yang paling sesuai dengan teknik spektrofotometri tampak. Teknik ini dipilih kerana penentuan timah dengan teknik spektrofotometri serapan atom (AAS) dengan menggunakan nyalaan termaklum banyak memberi masaalah. Walau bagaimana pun AAS dengan menggunakan relau grafit telah juga dikaji kerana keputusan yang lebih memuaskan dapat diperolehi dengan kaedah ini. Kaedah-kaedah yang lazim digunakan juga dilakukan untuk tujuan perbandingan.

Kaedah spektrofotometri tampak dalam menentukan kandungan timah dalam aloi dengan menggunakan 'catechol violet' dan 'cetylpyridinium bromide' telah dibincangkan dengan mendalam.

Asid oksalik dan asid laktik didapati dapat mempercepatkan proses pembentukan kompleks Sn-CV-CPB dan dari itu pertukaran warna dari dua jam ke anggaran tiga puluh minit.

Graf penentuan bagi kompleks timah ini adalah lurus hingga ke kepekatan timah setinggi 1.6 ppm pada panjang gelombang keserapan maksima 662 nm. Kepilihan kaedah ini bagaimana pun amat rendah bila diuji dengan aloi/logam piawai dari 'Bureau of Analysed Samples (U.K.). Beberapa langkah memperbaiki kaedah telah dibuat seperti pengasingan dan penopengan. Di antara langkah-langkah ini, keputusan yang menggalakkan telah didapati dengan gabungan kaedah pengasingan melalui pemendakan dan penopengan.

Teknik spektrometri serapan atom dengan relau grafit pula membincangkan tentang penentuan timah dengan menggunakan salutan zirkonium dan tungsten ke atas tiub grafit yang dikatakan boleh meninggikan kepekaan timah. Kecekapan tiub-tiub bersalut ini telah dibandingkan dengan kecekapan tiub-tiub grafit normal dan tiub-tiub pirolitik. Kesan pengubahsuai matriks dan agen penopengan juga telah dikaji. Ammonium hidroksida telah digunakan sebagai pengubahsuai matriks, manakala asid laktik, asid askorbik dan asid tartarik telah didapati berkesan sebagai agen penopeng. Pengatoman dari pelantar L'vov juga telah dikaji dan didapati kepekaan timah bertambah dua kali ganda. Walau bagaimanapun kejituan masih lagi tidak memuaskan (5-6 peratus).

Kaedah titrimetri dan gravimetri telah juga dikaji bagi tujuan perbandingan. Untuk titrimetri dua kaedah yang biasa telah digunakan iaitu pentitratan kompleksometri dengan menggunakan EDTA dan pentitratan iodometri yang menggunakan larutan piawai iodin untuk mengoksida timah(II) ke timah(IV).

Bagi gravimetri pula, timah telah dimendakkan sebagai asid metastannik dan, setelah dibakar dalam relau pada suhu 1000 °C, ditentukan sebagai stanum oksida (SnO_2).

Perbandingan yang berdasarkan kepada kejituan, kepekaan, ketepatan dan keringkasan tiap-tiap teknik yang telah diujikaji telah dibincangkan. Di antara teknik-teknik tersebut, bagi sampel-sampel yang dianalisis dalam projek ini, teknik spektrofotometri telah didapati paling baik dari segi ketepatan dan kejituan.

CHAPTER 1

INTRODUCTION

GENERAL INTRODUCTION

Tin in alloys has been determined most commonly by either gravimetry (Vogel, 1978; Gilbert, 1962; Wilson, 1962; Kolthoff, 1961) or titrimetry (Vogel, 1978; Gilbert, 1962; Wilson, 1962; Kolthoff, 1961; Dixon, 1962; Furuya, 1963; ASTM, 1972). Gravimetric methods for tin are normally subjected to errors caused by adsorption, co-precipitation or occlusion of other elements present and may require elaborate separation or purification of the final oxide (Vogel, 1978; Gilbert, 1962; Kolthoff, 1961). The titrimetric determination based on oxidation to the quadrivalent state by means of a standard iodate solution is definitely superior but very tedious and complete reduction of tin to the bivalent state and subsequent prevention of oxidation to tin(IV) (Vogel, 1978; Nobuhiko, 1983 and Kinnunen, 1957) really demand for special care of apparatus. The other widely applied titrimetric method involves complexing the tin with ethylene diamine tetraacetic acid (EDTA) (Raoot, 1984, Kinnunen, 1957; Dixon, 1962) the excess of which is titrated against standard lead nitrate, $Pb(NO_3)_2$ solution using xylenol orange as the indicator. The tin is then released from its tin EDTA complex by sodium

fluoride at pH 5-6 and the liberated EDTA titrated against lead nitrate solution. The method, however, works well only with solders and with samples of high tin content (more than 50 percent w/w). Atomic absorption spectrophotometry is fast gaining popularity as an alternative method to determine tin at low levels because of its rapidity. But tin was proven to be very insensitive towards the flame mode (Thomerson, 1971; Burke, 1972; Headridge, 1972; Thornton, 1974) such that either extraction (Headridge, 1972; Thornton, 1974), distillation (ASTM, 1972) or an additional device (Fleming, 1976; Jia, 1985; Liu, 1985) had to be used. Atomisation from graphite furnace although seemed promising for a direct analysis since most of the matrix could be burnt off during the ashing step, is not without problems. The problems are mainly associated with the tendency of tin to form volatile compounds and to interact with the graphite surface (Thamba, 1979; Tominaga, 1979; Fritzsche, 1979; Regan, 1976; Vickrey, 1981, Luo, 1985; Volyn, 1984).

Tin can also be determined by visible spectrophotometric method that is by forming a coloured tin complex and determined by taking absorbance in the visible region. To date the most promising complexing agent for tin is phenylfluorone (Sandell, 1959; Bennet, 1959) but this reagent often gives rise to colloidal solutions when applied to tin determination in alloys (Ross, 1961). In addition the tin-phenylfluorone complex is not water soluble such that the determination is often done in alcoholic medium instead. Catechol violet, another complexing

agent for tin on the other hand forms water-soluble complex with tin and therefore is much easier to handle. The method using catechol violet, however, suffers from its lack of sensitivity due to the fact the reagent blank absorbs very strongly at the wavelength of maximum absorbance of the complex. Currently a lot of efforts have been put in to improve the method and this include the use of sensitizing agents like gum arabic, sodium lauryl sulphate and cetyl trimethyl ammomium bromide.

OBJECTIVES OF THE THESIS

The study is mainly concentrated on improving the current methods of determining tin in alloys with emphasis being placed on analytical factors like sensitivity, accuracy, precision, speed and simplicity and to compare with regard to these factors against established classical methods namely titrimetry and gravimetry. Two main techniques were used for this purpose i.e. visible spectrophotometry and graphite furnace atomic absorption spectrophotometry. These techniques were chosen due to their wide usage in chemical analysis.

SUMMARY OF PRESENT WORK

The work was divided into three sections namely spectrophotometry, graphite furnace atomic absorption spectrophotometry and classical analysis, i.e. titrimetry and gravimetry.

Spectrophotometric Method

Tin was determined as Sn-CV complex.

The effects of two different surfactants namely cetyl pyridinium bromide (CPB) and alkyl phenyl polyethylene glycol (TRITON) on the absorption maximum of the complex were studied.

The method using CPB as the dispersant is a modification of other published methods and was tested on some certified reference materials with varying tin content from the Bureau of Analysed Samples Limited (BAS).

Several methods of eliminating the effects of interfering ions were also tried and the results compared. These include:

1) Masking of Interfering Ions Commonly Found in Alloys

Masking agents used are specific except when only small amounts of interfering ions were present (less than 1 percent) where lactic acid was found adequate. Tartaric acid was found effective in masking large amounts of lead and antimony, ascorbic acid for iron and thiourea or maleic acid for copper and nickel.

2) Combination of The Two Methods that is Separation Followed by Masking

a) separation by simple precipitation of the major interferent followed by masking.

Lead in the Pb-base white metal is separated as $PbSO_4$, copper as Cu-thiourea, iron in steel and foundary iron as $Fe(OH)_3$.

b) separation of tin from other matrix elements by solvent extraction using:

i) toluene.

Tin in the sample was extracted into toluene as tin(IV) iodide from a strongly acidic solution (sulphuric acid 8M) containing 0.1M potassium iodide. The tin extracted was then back-extracted into aqueous media using sodium hydroxide solution (50 percent v/v) and then acidified by quickly running the aqueous layer with constant stirring into a highly acidic solution of hydrochloric acid (5M) to give a final pH of approximately 1.5 before proceeding with colour development. This method, however, gave very poor results and poor recovery factor probably due to serious hydrolysis of tin occuring when the pH was changed first from acidic to alkaline and later back to acidic.

ii) trioctylphosphine oxide (TOPO) in cyclohexane

In this case tin was extracted from acidic solution of hydrochloric and sulphuric acid

mixture as tin (IV) chloride. The cyclohexane extract containing the tin was evaporated to get rid of the solvent and the residue redissolved in hydrochloric acid (10 percent v/v). Compared to the method of extraction using toluene, this method is of course superior, evaporation of the organic solvent proved to be much simpler than back extraction. However, the accuracy of the results obtained were only comparable to the method of masking only (Method A). Method B ii) : separation by simple precipitation followed by masking still gave the best and most accurate results.

Atomic Absorption Spectrophotometric Method

Several approaches of wall and platform atomisations were tried using different kinds of tube furnaces namely ordinary graphite as well as pyrollitic, tungsten (W) and zirconium (Zr) coated tubes. Comparison with regard to accuracy, precision, sensitivity and tube performance were carried out with the certified reference materials. Poor precision and accuracy were recorded with uncoated graphite tube but with coated and pyrollitic tube the performances were comparable, however, longest life of tube was recorded with using pyrollitic tube, more than 100 injections against about 50-60 injections with tungsten and zirconium coated tubes under the conditions used in this work.

Better sensitivity was obtained with Standard Temperature Platform Furnace (STPF) method but precision was only slightly improved. Analysis of tin using platform atomisation, thus could turn out to be very costly considering the short life and the cost of the platform which presumably is about that of the tube at the conditions of this work.

Gravimetry and Titrimetry

These classical methods were carried out for comparison purposes. Emphasis was placed on analytical aspects like accuracy, speed and simplicity against the investigated methods. Only the widely applied methods for analysis of alloys were carried out, i.e.

1. Titrimetry

Complexometric titration of Sn(IV) with EDTA using xylenol orange as indicator and iodometric titration of Sn(II) using starch as indicator.

Complexometric titration only worked with samples of high tin content like tin base metal and solders. It is not suitable for alloys that contain too much copper like brass and iron like steels and foundary iron. Iodometric method also worked well with samples of high tin content and samples that do not contain appreciable amounts of lead and antimony which gives rise to serious interference problems.